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TITLE: DIRECT SPECIATION OF METAL AND METALLOID IONS BY OPTICAL SPECTROSCOPIES

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Direct Speciation of Metal and Metalloid Ions by Optical Spectroscopies

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Chemical interactions between dissolved organics and mineral surfaces have been increasingly the focus of investigations of diagenetic processes in sedimentary basins and in oil fields. These interactions can significantly influence the release, sequestering and transport of metals in low- to moderate-temperature hydrothermal ore systems such as the Mississippi Valley Type (MVT) deposits, and be a critical component of creation, destruction and reorganization of permeability through complex formation with the metalloids Si and Al. Our recent efforts have concentrated on organic-metalloid interactions because of their importance in rock alteration/weathering and in primary and enhanced oil recovery (EOR) processes.

Molecular level spectroscopic investigations of organic/inorganic interactions provide important new information on sedimentary geochemistry through the identification of interactions over moderate temperature and pH ranges. Although the official title of this project indicates the use of only optical spectroscopies, a combination of Uv/Vis/IR absoption, Raman scattering, and ^{29}Si and ^{13}C nuclear magnetic resonance (NMR) experiments are actually employed. A major advantage of integrating spectroscopic results with diagenesis studies is the ability to directly examine the mechanisms of interactions, even in complex matrices and with competing processes. Furthermore, we are extending these techniques to probe fluid inclusions with micro Raman and luminescence techniques to directly compare laboratory results with natural reservoir systems.

The mobility and transport of silica in natural waters has been a subject of debate for over a century (JULIEN, 1879; ILER, 1979). Field studies have found direct correlations between dissolved organic carbon (DOC) and dissolved silica in soil pore waters (CHESWORTH and MACIAS-VASQUEZ, 1985; WILLIAMS et al., 1985), lake and marine sediment pore waters (ASTON, 1983), shale pore waters (LERMAN, 1979), oil field formation waters (SURDAM et al., 1984), and oil-contaminated shallow groundwater (BENNETT and SIEGEL, 1987). This latter field study was especially important because it also correlated quartz etching under neutral pHs with DOC concentration. Therefore, matrix-destroying complexation of other rock-forming cationic

constituents, especially Al, could not be invoked. The DOC's implicated in these correlations consist primarily of complex organic acids, including aromatic, keto- and hydroxy-acids, and other partially oxidized carbon species (AIKEN, 1987;BAEDECKER et al., 1987). Enhanced silicon mobility is thought to involve either an increase in proton availability from these acids or significant organo-silica interactions.

Decreased pH due to organic acids cannot account for the increased silicon mobility and quartz etching found in the near neutral (pH=6 to 7) oil-contaminated groundwater site near Bemidji, MN (BENNETT and SIEGEL, 1987), thereby implicating organo-silica interactions. These interactions may include hydrogen bonded charge transfer complexes as well as covalently bonded structures (ILER, 1979), although reliable direct evidence of these interactions is rare (FARMER, 1986; EVANS et al., 1990). Laboratory work by BENNETT et al. (1988) and BENNETT (1991) show that only poly-functional organic acids increase the dissolution rate of quartz and the final solubility of the mobilized silicon, so our studies have primarily focused on oxalate and citrate anions. Oxalate is the simplest difunctional acid anion and is also found naturally in concentrations of up to 3 mM in oil field brines (KHARAKA et al., 1984, 1987), while citrate is produced in significant quantities biologically and can exist in local environments, especially in soils near rock-weathering fungi. Furthermore, citrate is more active in mobilizing silica than oxalate (BENNETT et al., 1988). Other naturally occurring acids such as fulvic and humic acids are also implicated in silicon mobilization, but are too complex for these initial spectroscopic studies.

In a previous paper, Raman scattering and infrared absorption experiments purported to show spectroscopic evidence for a strong, covalently bonded silicon ester formed between oxalate and silicic acid (soluble silicon source) (MARLEY et al., 1989). As these experiments were only done at room temperature and at neutral pH, we decided to pursue them to examine the range of conditions in which this silicon ester could be expected to form. A diagnostic vibrational peak at 1305 cm^{-1}, both Raman and IR active and attributed to ν_{C-O-Si} (MARLEY et al., 1989), was used as the ester marker. This marker was observed in the IR when $4 < pH < 12$, and also showed no dissociation to at least 125°C. In fact, the spectrum was qualitatively unchanged to 175°C, but leakage from the cell precluded any quantitative conclusions. This temperature stability was considered especially important because organics in oil field brines and sedimentary basins in general exist between 85 and 200°C (i.e. between the temperatures at which organic-consuming bugs are significant and at which the organics decarboxylate - KHARAKA et al., 1984, 1987). Furthermore, this is also the temperature range of MVT deposit formation. However,

^{13}C NMR studies performed to corroborate the bidentate nature of the oxalate interaction with silicon did not revealed a ^{13}C chemical shift between pure oxalate and oxalate/silicic acid solutions (Figure 1), implying that any complexation must be below the NMR detection limit. Subsequent IR and Raman control experiments involving oxalate-only solutions also detected the 1305 cm^{-1} "marker" peak (Figure 1). Moreover, when we went back to the original paper (MARLEY et al., 1989), we discovered that the published control experiments involved oxalic acid rather than oxalate! Our experiments to determine the environment under which a silicon ester could exist instead turn into experiments that show where no detectable ester (or any other covalently bound Si-oxalate) is observed. Because silicon oxalate ester bond formation may be expected to strengthen at higher temperatures (see Al-oxalate data below), the negative findings from elevated temperature experiments are nonetheless a significant contribution.

In order to improve our detection limit to see if any significant organic-silicon interaction can occur, we have turned to ^{29}Si NMR experiments. These experiments probe the chemical environment of the Si atom rather than the organic carbons, and hence allow us to try to push the equilibrium toward complex formation by using excess organic species. Near-neutral solutions of ^{29}Si (introduced as enriched $^{29}SiO_2$ below the concentration that would result in dimerization / polymerization) and oxalate/citrate ligands were allowed to sit at room temperature for two months. Figure 2 shows the room temperature spectra for 2 mM Si alone and with 50 mM citrate or oxalate. No obvious new peak appears in the organic containing solutions, although a small hump possibly appears at ~-50 ppm in the oxalate spectrum. Therefore, no definitive evidence for a silicon ester is found, either because it is below the detection limit of the spectrometer, close to the detection limit (if the -50 ppm peak is real), or it is buried under the host Si peak at -116 ppm. However, these experiments are continuing, and, because they are new and an interpretational database has not yet been established, no final conclusions can yet be drawn from them . A striking feature of the spectra is the broadness of the parent Si peak (21 ppm or 1046 Hz), indicating exchange of the deuterium on $Si(OD)_4$ and D_2O solvent, where D_2O was used to provide an NMR signal "lock" to eliminate any signal drift problem. Because the broad signal implies either intermediate exchange kinetics or multiple species (dimers, trimers, etc.) with unresolved peaks, the temperature was both increased (52°C) and decreased in an effort to narrow the signal by entering the slow or fast exchange regimes. Furthermore, the $Si(OD)_4/D_2O$ sample has also been diluted by a factor of 10 with H_2O to try to eliminate the possibility that dimers/polymers contribute to the peak broadness. Not all of this data has been analyzed yet. However, the fact

that 200 μM Si species can be observed with NMR is remarkable as it is a directly relevant environmental concentration. For example, [Si] in the Rio Grande reaches concentrations of 320 μM.

Besides silicon(IV), aluminum(III) is another major cationic constituent of rock and soil matrices. Aluminum is known to form multiligand complexes with oxalate at room temperature (BOTTARI and CIAVATTA, 1968; SJOBERG and OHMAN, 1985; THOMAS et al., 1991). In fact, oxalate solutions can leach aluminum from the relatively insoluble solid Al_2O_3 by stirring a slurrey with sodium oxalate at near neutral pH's (between 5 and 8). Aluminum-oxalate peaks are found in both IR and Raman spectra. Besides increasing the weathering of silicate minerals and consequently affecting geochemical cycles, biochemical cycles may also be affected by the simultaneous liberation of toxic Al and nutrients such as Fe, Ca, K, and Mg from mineral matrices (SJOBERG and OHMAN, 1985).

The effects of Al complexation by oxalate are easily followed spectroscopically, in contrast to the difficulty presented by Si complexation described above. Specifically, we have initiated experiments to determine the temperature dependence of Al-oxalate species, particularly to the moderate temperature regime relevant to sedimentary basins. As a pre-requisite, we first had to determine the spectroscopic signatures of the individual $Al(ox)_n^{3-2n}$ species. This process has been aided by previous room temperature speciation studies, mostly based on potentiometric results, which defined experimental conditions dominated by different complexes. Figure 3 shows the results of modifying the Al/oxalate ratio on the spectra. Since the log of the step-wise association constants for $Al(ox)^+$, $Al(ox)_2^-$, and $Al(ox)_3^{3-}$ are 6.0, 5.0, and 4.0 respectively (BOTTARI and CIAVATTA, 1968; SJOBERG and OHMAN, 1985), the 1428 cm^{-1} peak seen to dominate at oxalate/Al ratios > 3 can be assigned to $Al(ox)_3^{3-}$, while the peak at 1408 cm^{-1} can be assigned to $Al(ox)_2^-$. A peak associated with $Al(ox)^+$ can not be definitely assigned, either because it is weak or buried beneath other peaks. The assigned peaks represent coordinated oxalate vibrations (major contributions from C-O and C-C stretches) with different force constants due to Al complexation. Peak assignments are also consistent with changes in oxalate availability as a function of pH (SJOBERG and OHMAN, 1985).

The major solution effect of increasing temperature is the decrease in solvent dielectric constant (BRIMHALL and CRERAR, 1987; SEWARD, 1984). Highly charged species are therefore destabilized relative to lower charged ones, and stability constants change to reflect this. Therefore, when conditions were set for equal concentrations of $Al(ox)_3^{3-}$ and $Al(ox)_2^-$ at room temperature, we expected an increase in

temperature to lower the concentration of the highly charged $Al(ox)_3^{3-}$ species. However, Figure 4 shows no change in the populations of the two species, implying an increase in the association constant for $Al(ox)_3^{3-}$. This is even more remarkable when the lower availability of oxalate is taken into account in this pH=3 solution, as $logk_2$ for oxalic acid increases from -4.29 at 25°C to -4.42 at 50°C and -4.69 at 80°C. Therefore, our emphasis has shifted to competition studies for oxalate as temperature is changed. For sedimentary basin geochemistry, a competing cation such as zinc, calcium, or iron could be tried. The oxalates of the first two, however, are not soluble enough for spectroscopic examination, so we will continue our experiments with Al(III) and Fe(III) competition for oxalate.

With enhanced understanding of rock matrix - organic interactions and spectral signatures of these interactions provided by the laboratory analogue studies, we intend to pursue investigations of organic species in fluid inclusions in sedimentary basins such as the oil-producing Austin Chalk. Geochemical issues of importance include thermal maturation and porosity of the surrounding rock matrix, petroleum migration history, and interactions of enhanced oil recovery (EOR) techniques. Fluid inclusions allow us to study these issues because they preserve the paleo-chemistry of the fluids that led to oil field development and contain the well-equilibrated fluid/mineral surface environment that is needed to predict the effects of EOR techniques. A range of temperatures is also readily accessible. Toward this end, we are acquiring a Raman microprobe accessory to allow examination of the vibrational fingerprints of organic species in inclusions down to 5 microns in size, and also the monochromator attachments for a UV adapted microscope to allow us to use synchronously scanned fluorescence. This latter technique has recently been used with macroscopic samples to add molecular specificity to sensitive luminescence measurements (PHARR et al. 1991; PHARR, 1991; CABANISS, 1991), and will be adapted here to microscopic measurements to probe the organics in fluid inclusions. The combined application of Raman microprobe and fluorescence will provide important cross checks. Demonstration of microscopic scale results will allow investigations of a diverse range of problems, including paleochemistry / paleoclimate of Yucca Mountain and ore-deposits in geothermal systems such as Carlin type gold deposits with organic-rich fluid inclusions (Jeff Hulen, Univ. of Utah, personal communication). Note that organics are unexpectedly present and largely ignored components in some geothermal systems such as the Valles Caldera drillcore fluid inclusions (MUSGRAVE and NORMAN, 1991; MUSGRAVE et al. 1991). Organic species are also often discussed but little quantified in many other systems, particularly with respect to potential coupled interactions with metals and metalloids which are direct applications of this work.

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FIGURE CAPTIONS

1.(a) FTIR spectrum of a sodium oxalate / silicic acid mixture at neutral pH and the corresponding spectrum of sodium oxalate with no added silicon (inset, on different horizontal scale). The 1308 cm^{-1} peak is therefore not diagnostic of silicon ester formation as concluded by MARLEY et al. (1989). (b) Carbon-13 FT-NMR spectrum of a sodium oxalate / silicic acid mixture at neutral pD and the corresponding spectrum of sodium oxalate with no added silicon. (Because the spectra were obtained in D_2O to provide a frequency lock from deuterium to prevent frequency drift, pD is noted rather than pH). The identical chemical shifts argue for identical chemical environments for the oxalate carbons - namely, one not involved in a strong covalent bond with the silicon compound.

2. Room temperature ^{29}Si NMR spectra of (from bottom spectrum to top) 2 mM $^{29}Si(OD)_4$ (from an enriched 97% $^{29}SiO2$ silicon source) with no organic ligand (pD=6.7), 2 mM $^{29}Si(OD)_4$ / 50 mM sodium citrate (pD=7.4), and 2 mM $^{29}Si(OD)_4$ / 50 mM sodium oxalate (pD=7.4). Note that the spectra were taken in D_2O to provide a frequency lock to prevent signal drift, and that neutral D_2O has a pD of 7.5. For our 250 MHz spectrometer, we used a 10 µsec pulsewidth (180^{o} pulsewidth measurement for $Si(OD)_4$ was determined to be 43 µsec), a relaxation time of 90 seconds (T_1 for silicon is notoriously long), and an acquisition time of 0.82 sec. The lack of significant spectral change, despite the excess organic ligand, demonstrates the weakness (or extremely slow kinetics) of any chemical reaction between the silicic acid and organic bases.

3. Raman vibrational spectra from solutions of different Al^{3+} / $oxalate^{2-}$ concentration ratios at near neutral pH. Note that at near neutral pH, there is considerable precipitation for the (1:1) and (1:2) samples, as well as the presence of other Al-oxalate species such as $Al_2(OH)_2(Ox)_2$ and $Al_3(OH)_3(Ox)_3$ (SJOBERG and OHMAN, 1985). These additional species may be the cause of the 1449 cm^{-1}

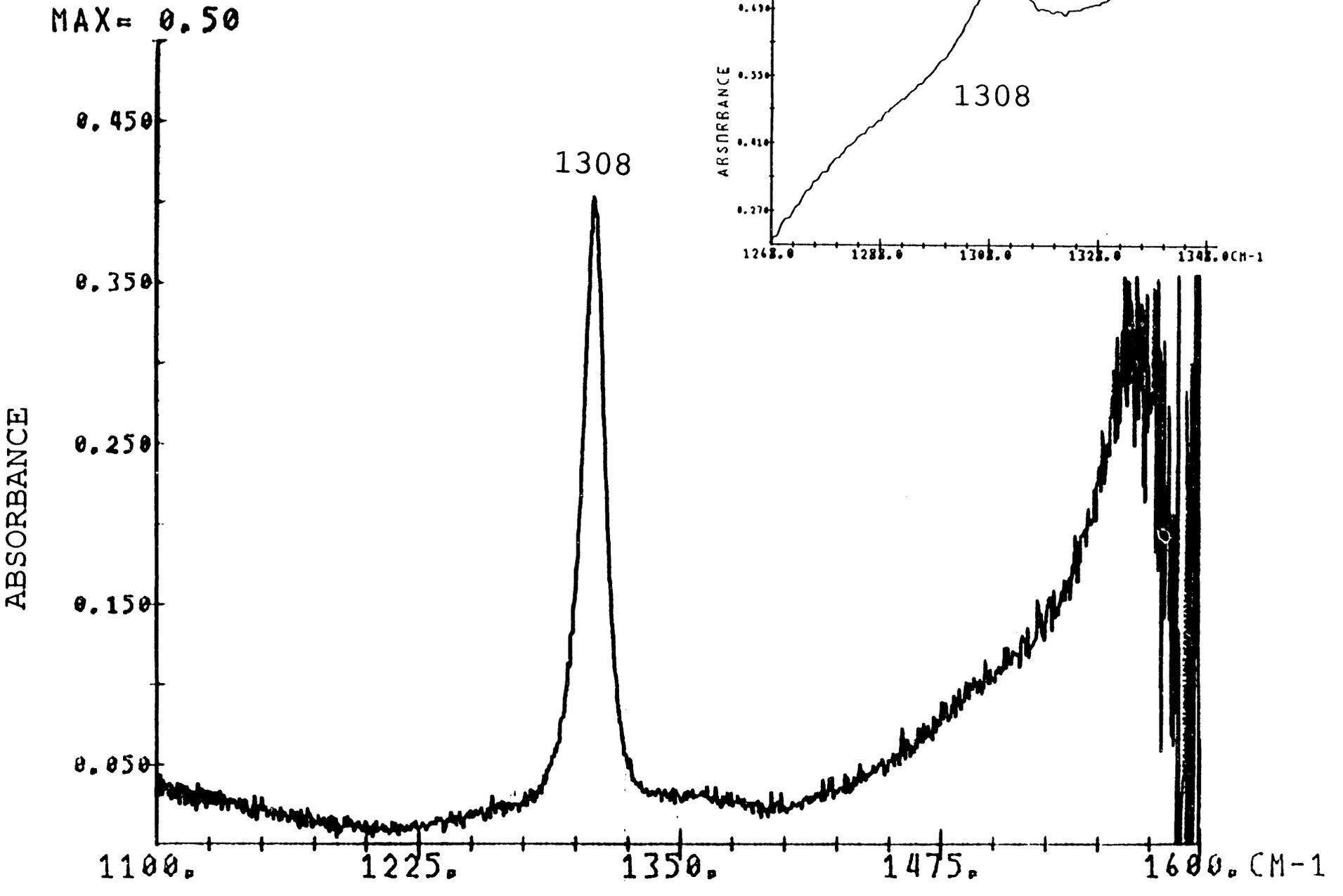
peak observed only at these concentration ratios. The peaks at 1408 cm^{-1} and 1429 cm^{-1} are assigned to oxalate vibrations from $Al(Ox)_2^-$ and $Al(Ox)_3^{3-}$ respectively.

4. Temperature dependent Raman spectra for a solution of 20 mM Al^{3+} / 50 mM oxalate at pH=2.9. Under these conditions, the ratio of $Al(Ox)_2^-$ to $Al(Ox)_3^{3-}$ is 1 at 25°C (SJOBERG and OHMAN, 1985). Although the 1429 cm^{-1} peak from $Al(Ox)_3^{3-}$ was expected to lose intensity relative to the 1408 cm^{-1} peak of $Al(Ox)_2^-$ as the temperature was increased, the spectra show a lack of change with temperature, indicating that the third association constant ($Al(Ox)_2^- + Ox^{2-} \rightarrow Al(Ox)_3^{3-}$) actually increases with temperature, despite the high charge of $Al(Ox)_3^{3-}$ and the lower availability of oxalate at higher temperatures.

INFRARED ABSORPTION SPECTRA

Silicic Acid / Oxalic Acid Mixture

pH = 8.7



Sodium Oxalate (no Silicic Acid)

pH = 8.2

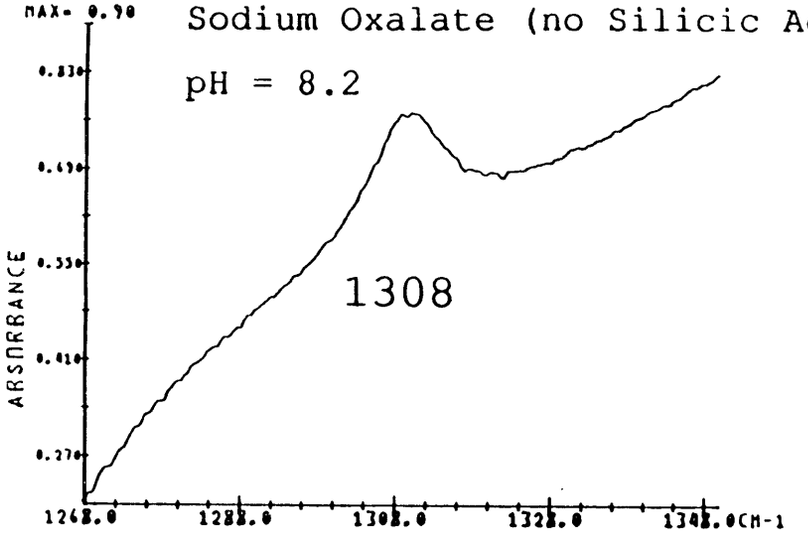
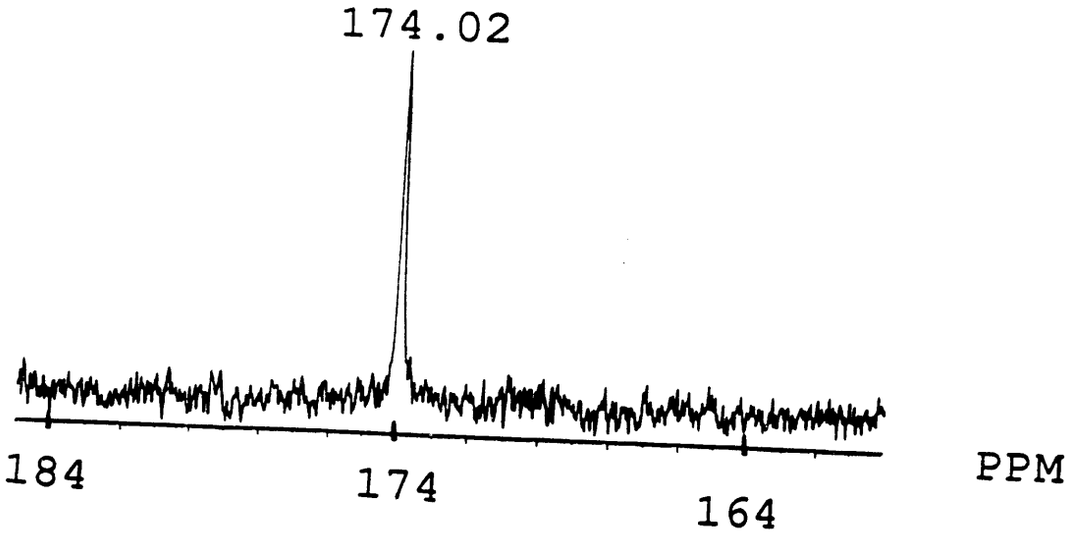


Figure 1a

NMR SPECTRA

Silicic Acid / Oxalic Acid Mixture
pD = 8



Sodium Oxalate (no Silicic Acid)
pD = 8

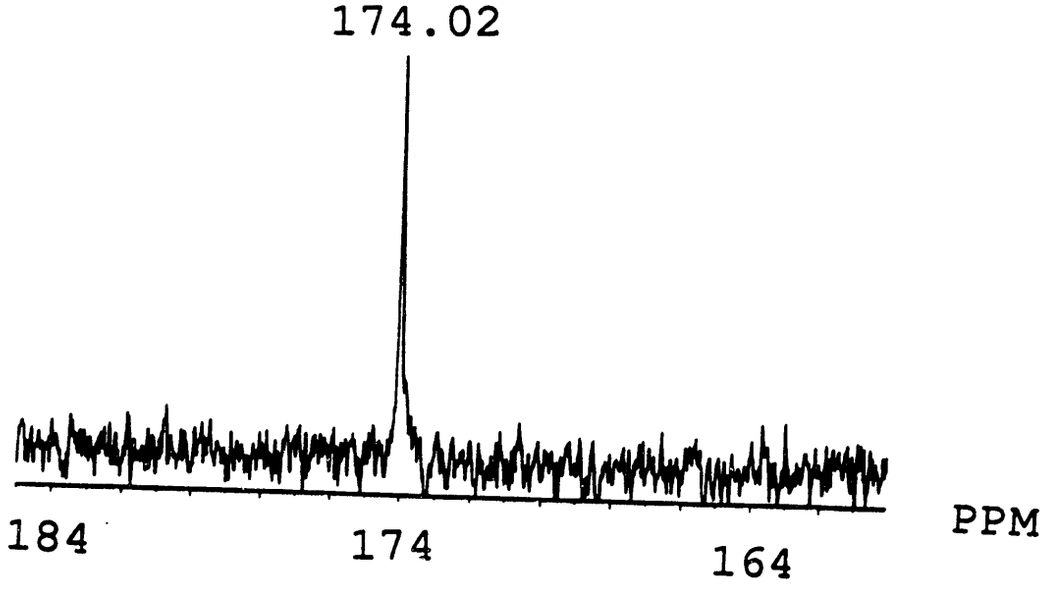


Figure 1b

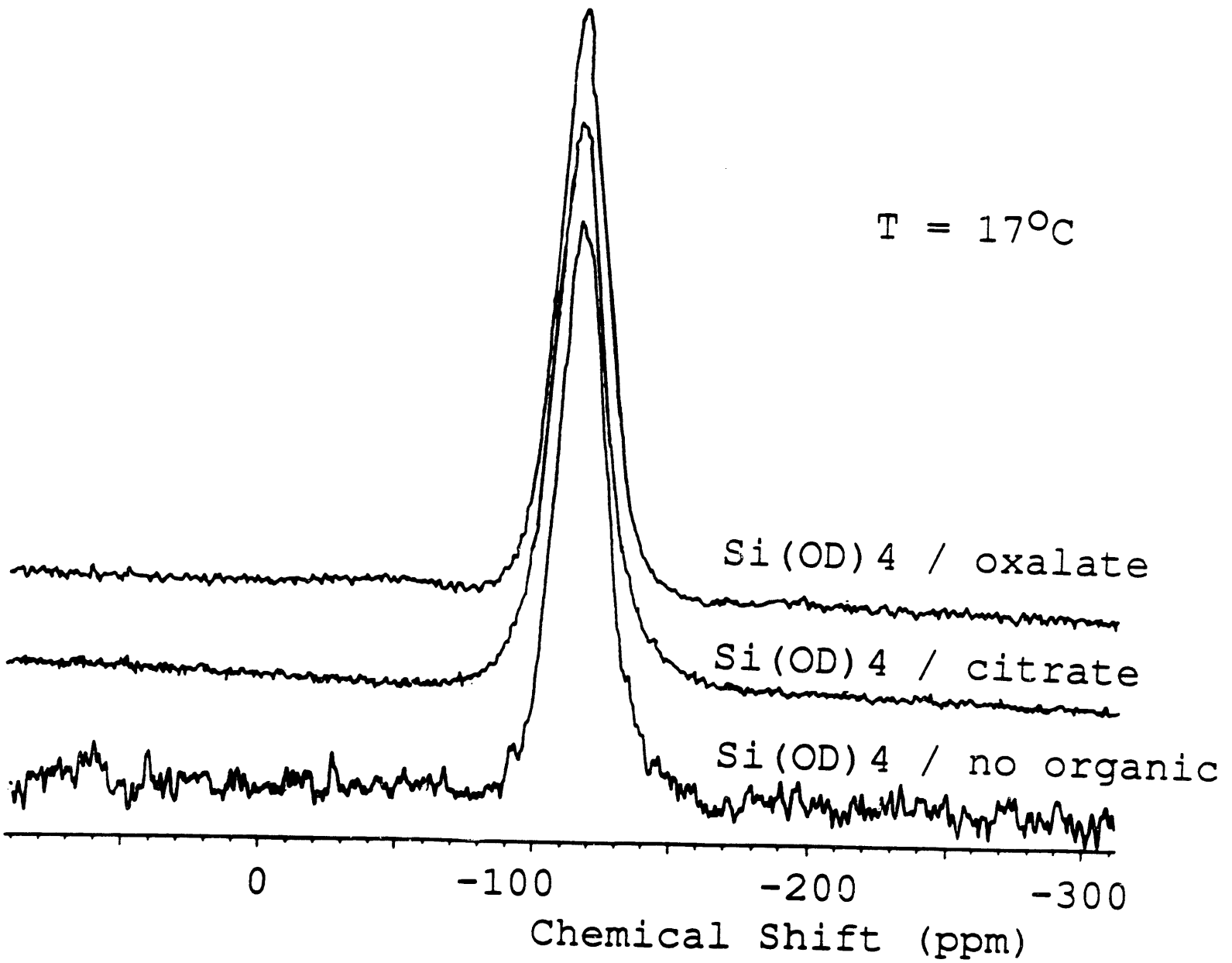

T = 17°C
Si(OD)4 / oxalate
Si(OD)4 / citrate
Si(OD)4 / no organic
0
-100
-200
-300
Chemical Shift (ppm)

Figure 2

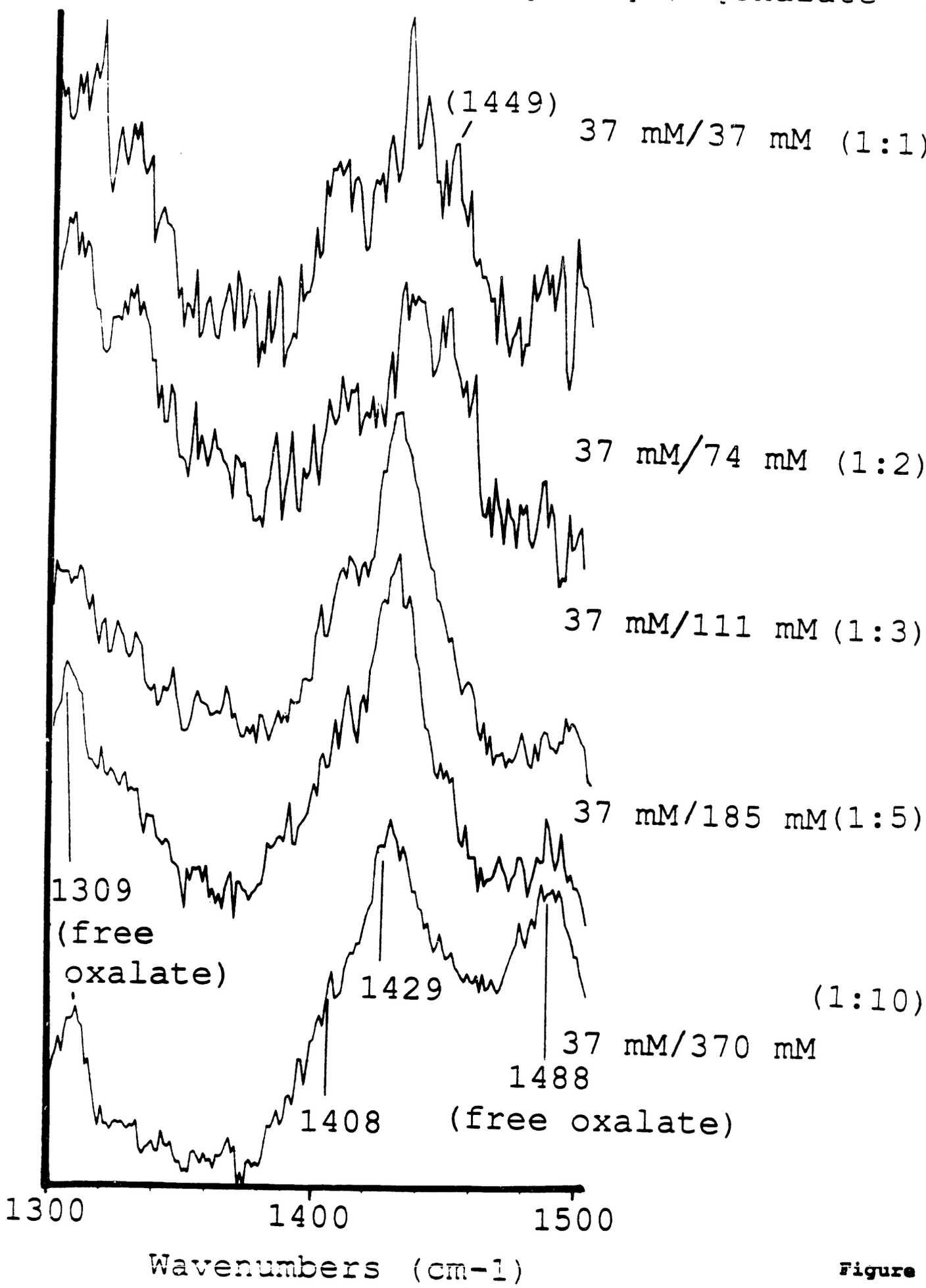

[Al3+] / [oxalate2-]
(1449)
37 mM/37 mM (1:1)
37 mM/74 mM (1:2)
37 mM/111 mM (1:3)
37 mM/185 mM(1:5)
37 mM/370 mM
(1:10)
1309
(free
oxalate)
1429
1488
(free oxalate)
1408
1300
1400
1500
Wavenumbers (cm-1)

Figure 3

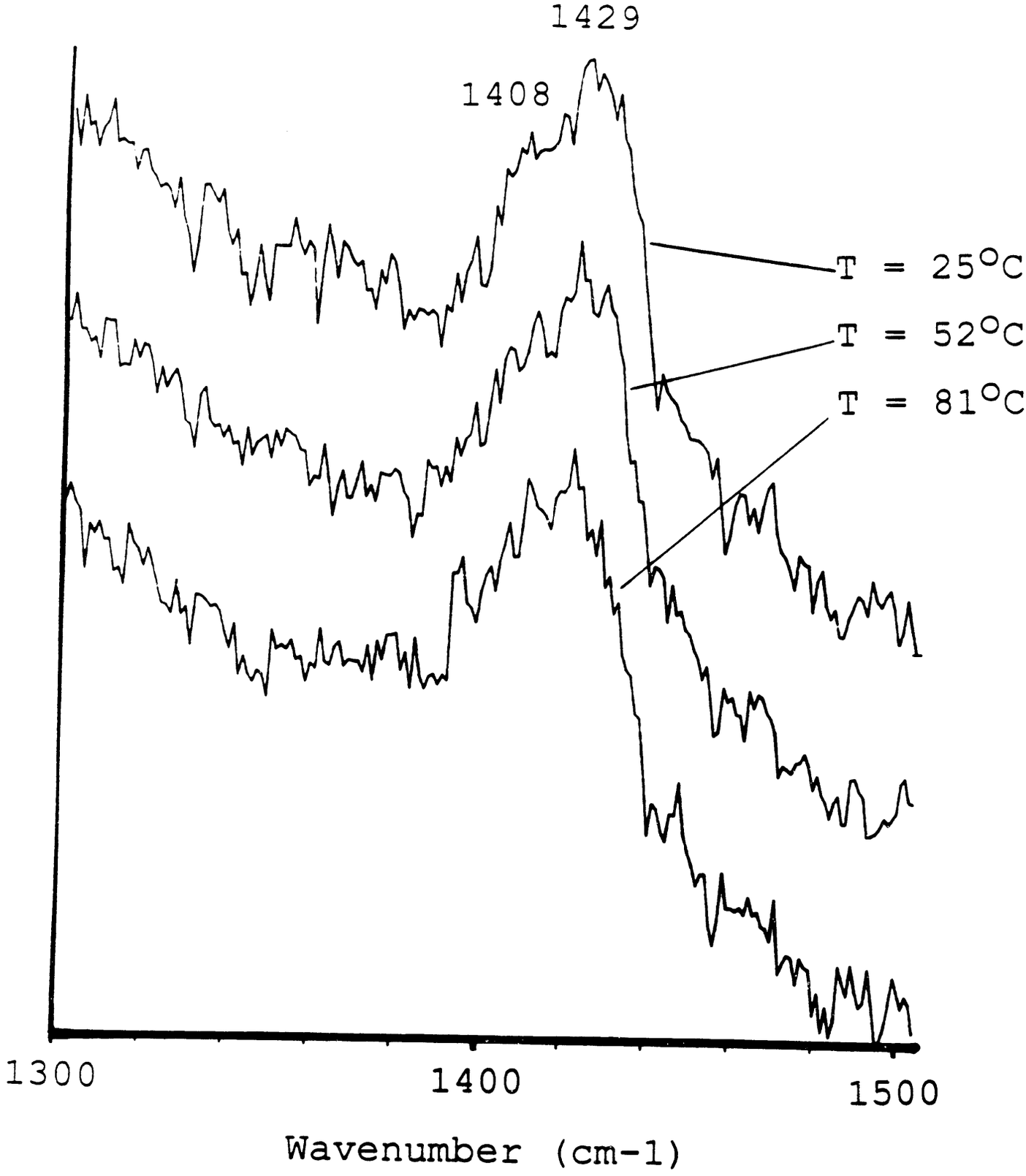


Figure 4

END

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